DIELECTRIC CONSTANTS OF SOLUTIONS CONTAINING ASSOCIATING MOLECULES

BY
CARL BERNARD KRETSCHMER
A.B., University of Colorado, 1938

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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DIELECTRIC CONSTANTS OF SOLUTIONS CONTAINING ASSOCIATING MOLECULES

Theoretical

The theory of dielectric polarization developed by Debye in 1912[1] has been widely used to calculate dipole moments from measurements of the dielectric constants of dilute solutions. It has of course been recognized that Debye's equation is not exact at any finite concentration, because of interaction between dipoles. Therefore the usual procedure has been to calculate the apparent molal polarization of the polar solute over a range of concentrations and to use the extrapolated value at zero concentration. The apparent molal polarization of alcohols in dilute solutions in non-polar solvents has been found to pass through a minimum and often also a maximum. It has not been possible to formulate a satisfactory explanation of this complex behavior in terms of association, chiefly because the Debye theory does not take account of the strictly electrostatic interactions of dipoles in solution.

Onsager has recently developed a theory[2] based on a model which is necessarily greatly simplified, but which recognizes explicitly the effect of a permanent dipole on the internal field. Applied to a solution of a polar substance in a non-polar solvent, this analysis yields an equation which has a limiting form at infinite dilution similar to that of the Debye equation. Dipole moments calculated from this limiting form do not differ markedly from those calculated by the former procedure. Onsager's equation, however, is a much better approximation than the Debye equation at finite concentrations, and accurate values of the dipole moment can be calculated by using the complete equation rather than its limiting form. In this way the uncertainties of the extrapolation to infinite dilution may be avoided. In cases where association occurs the Onsager equation can be used to calculate the mean

squared effective moment per molecule, giving a quantitative measure of the effect of association as distinguished from merely electrostatic interaction. The formation of polymers of n molecules will cause this quantity to be greater or less than its value at infinite dilution according to whether the moment of the complex is greater or less than the square root of n, times that of a single molecule.

Results and Discussion

Dielectric constants and densities of solutions of eight compounds in carbon tetrachloride or benzene were determined over a range of concentration and temperature, using a heterodyne beat apparatus. Capacities were measured by a substitution method which eliminated the necessity of maintaining the oscillators at a constant frequency for more than a few minutes. The cell used consisted of three concentric platinum cylinders sealed into a Pyrex envelope. The substances studied, with their moments as calculated from the limiting form of the Onsager equation, follow:

Secondary butyl alcohol	1.76×10^{-18} e.s.u.
Tertiary butyl alcohol	1.71
Benzyl alcohol	1.73
Diethylisopropylcarbinol	1.70
Phenol	1.44
Normal butylamine	1.39
N-*n*-butylacetamide	1.46
Aniline	4.00

These values agree with those previously determined by the conventional procedure. Values calculated from the complete Onsager equation for several of the substances studied agree within two per cent with those listed above. For aniline the agreement holds up to a concentration of 0.15 mole fraction, demonstrating the validity of the Onsager equation for an unassociated solute at mole fractions up to 0.15.

If there is no association, the molal dielectric suscepti-

bility, $(\epsilon\text{-}1)\ v/4\pi$, must decrease with rising temperature, because the increased thermal agitation reduces the orienting effect of the applied field. All the alcohols studied had the opposite behavior within a concentration range starting at about 0.05 mole fraction. This behavior can be attributed to the formation of cyclic dimers through hydrogen bonding, with small or zero moments, the effect of rising temperature in breaking up these complexes being great enough to overbalance the reduced orientation. At some higher concentration the temperature variation again becomes normal, because of increasing formation of linear polymers of the third and higher orders. Unlike the cyclic dimers, the linear polymers are formed with increasing difficulty as the group attached to the -OH is made more branched. Accordingly this second inversion is found at 0.13 mole fraction for normal butanol,[3] at 0.25 for secondary butanol, and at about 0.50 for tertiary butanol. Steric hindrance is so great for diethylisopropylcarbinol that the second inversion is never reached at all; the pure alcohol has a positive temperature coefficient of dielectric constant. In this compound there is also some steric hindrance to the formation of the cyclic dimers, the first inversion occurring at 0.10 mole fraction. In benzyl alcohol solutions the inversion points occur at about the same concentrations as for normal butanol, but, because of the effect of the benzene ring, the positive temperature coefficient is much smaller, and the behavior is normal above 30°C.

Phenol solutions had a negative temperature coefficient of susceptibility at all concentrations, and there was no evidence of dimer formation of a type which either enhanced or diminished the susceptibility. At higher concentrations there was some indication of linear polymer formation. The explanation may be offered that, besides the cyclic dimers characteristic of the alcoholic -OH, other dimers are formed in which bonding takes place through an unshared electron pair on the carbon ortho or para to the -OH, which is present in certain of the resonance forms of molecules like phenol. The com-

bined effect of the different kinds of dimers could be such as to leave the mean squared moment per molecule nearly unchanged.

Up to a concentration of 0.15 mole fraction, normal butylamine and aniline showed no evidence of either kind of association. Apparently the greater basicity of the amino group makes hydrogen bonding much more difficult than for the alcohols. The nitrogen-substituted amide was greatly associated even at very small concentrations, the mean squared moment per molecule at 0.0237 mole fraction being 2.27 times its value at infinite dilution. In this compound the bonding must be between the amino group and the carbonyl oxygen, and the polymers must be predominatly linear rather than of the cyclic type which might have been expected by analogy with the carboxylic acids.

Lassettre[4] has given a method for calculating the dissociation constants of all the polymers existing in significant numbers in solution, from measurements of such properties as freezing point or vapor pressure. It was not possible to apply a similar method to the results of the present investigation, however, for the dielectric susceptibility depends on the moment of each polymer as well as upon its dissociation constant. If the dissociation constants were known from measurements of some colligative property, it would be possible to calculate the moment of each polymer from the dielectric constant data.

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VITA

The author was born at Pueblo, Colorado, on August 4, 1916. He received his elementary education in the public schools of that city and was graduated from Centennial High School in June, 1934. He attended the University of Colorado at Boulder from 1934 to 1938, receiving the degree of Bachelor of Arts in June, 1938. The author attended the Graduate School of the University of Illinois from 1938 to 1941, holding a University Scholarship the first year and University Fellowships the last two. He is a member of Phi Beta Kappa, Phi Kappa Phi, and Sigma Xi, and is co-author of an article entitled "Association of Phenols," *J. Chem. Physics, 9,* 284 (1941) with Professor W. H. Rodebush.

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